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Title: Simulation Study of the Elastic Mechanical Properties of HMX

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Simulation Study of the Elastic Mechanical Properties of HMX

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Thomas D. Sewell, Dmitry Bedrov, Grant Smith

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Results of calculations of the elastic mechanical response of crystalline HMX polymorphs are summarized. The work is based on atomistic molecular dynamics and Monte Carlo simulations. Principal achievements are: (1) prediction of room temperature and pressure elastic tensors for β-, α- and δ-HMX; (2) calculation of room temperature isotherms for each polymorph; (3) extraction of initial bulk modulus and pressure derivative from the isotherm; and (4) "discovery" of a pressure induced phase transition in α-HMX (preliminary result). Details of the work, and implications, will be discussed.

Simulation Study of the Elastic Mechanical Properties of HMX

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Goals of the Research

- Develop & apply molecular and coarse-grained methods to PBX constituents
  - grains, binder, and interactions between them
- Validate methods/potentials against data
  - *And extend intervals for which information is available*
- Make predictions where data do not exist
  - *Guided by needs of mesomechanics modelers*
    - *E.g., Menikoff and Sewell, Combustion Theory and Modeling 6, 103 (2002)*
    - *Focus on properties and states relevant to weak-shock initiation*
- Major focus today
  - *Atomistic calculation of elastic properties of HMX*

Potential-Energy Surface

- Forcefield due to Smith & Bharadwaj

$$V(\theta,\vartheta,\tau,R) = \tfrac{1}{2}\sum_{bends} k_\theta\left(\theta-\theta^0\right)^2 + \tfrac{1}{2}\sum_{wags} k_\vartheta\left(\vartheta-\vartheta^0\right)^2$$

$$+ \tfrac{1}{2}\sum_{torsions} k_\tau\left[1-\cos(n\tau)\right] + \sum_{nonbonds}\left[A\exp(-BR)-CR^{-6}+q_iq_jR^{-1}\right]$$

- Parameterized using literature values & B3LYP/6-311G**//MP2/6-311G** electronic structure calculations
- Valence parameters determined from gas-phase quantum studies of dimethylnitramine, 1,3-dimethyl-1,3-dinitromethyldiamine, and HMX
- Rigid covalent bonds; fully flexible otherwise
- Nonbonded parameters
  - Repulsion/dispersion: literature
  - Partial charges: symmetry, dipole-moment constrained integration of electron density
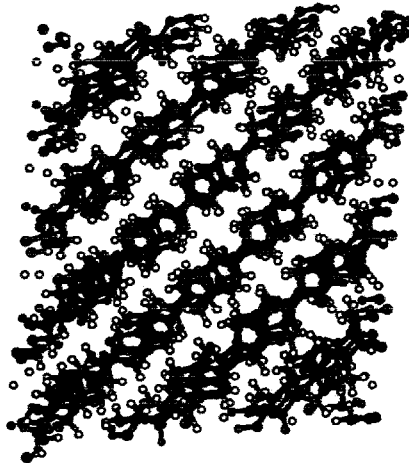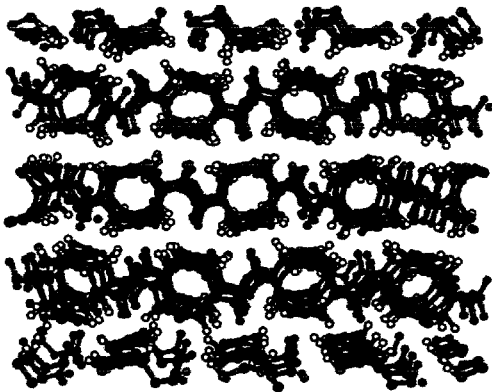- Validated against experimental crystal structures, CTEs, ΔH_s

Snapshots From the Simulations
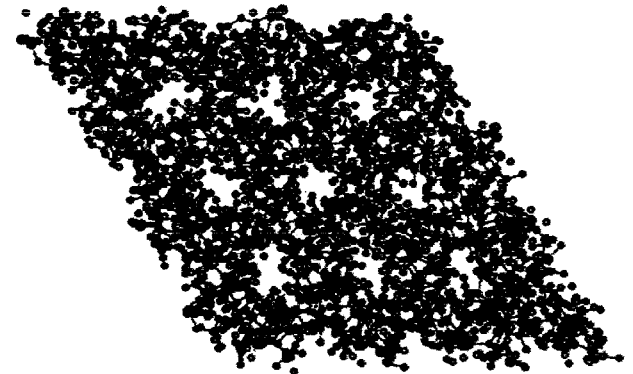
α-HMX
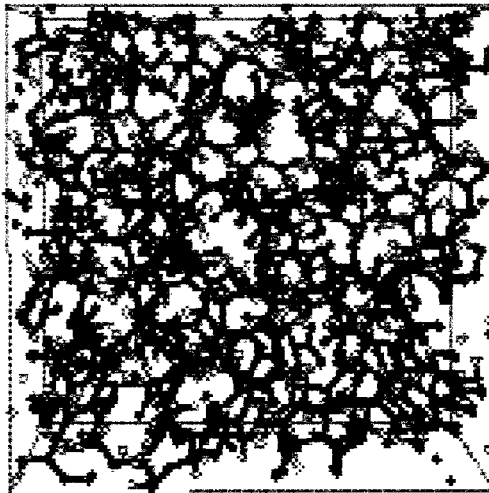64 molecules
8 unit cells
295 K

β-HMX
48 molecules
24 unit cells
295 K

δ-HMX
96 molecules
16 unit cells
295 K

Liquid HMX
48 molecules
700 K

Previously...

- ## Structural parameters, CTEs, heats of sublimation of crystal polymorphs
  - *J. Comput.-Aided Mat. Design (in press, June '02)*
  - *SCCM '01 Proceedings (Bedrov et al.)*

- ## Temperature-dependent shear viscosity, thermal conductivity, and self-diffusion coefficients of melt
  - *J. Chem. Phys. 112, 7203 (2000)*
  - *Chem. Phys. Lett. 324, 64 (2000)*

- ## Preliminary predictions of HMX elastic properties
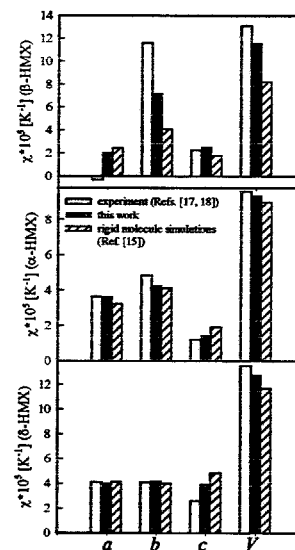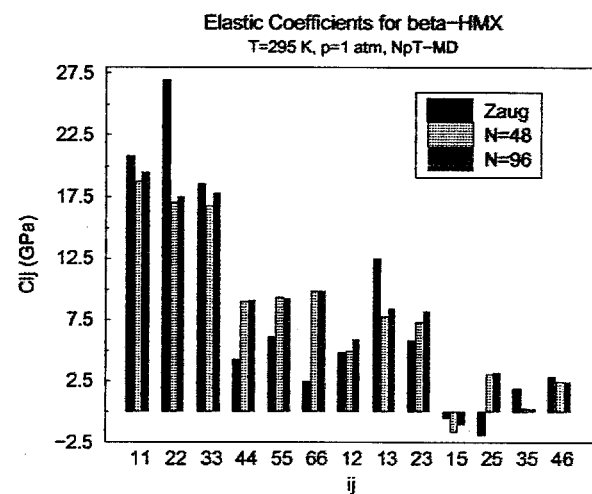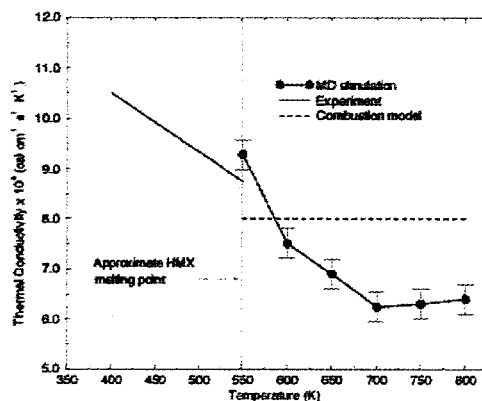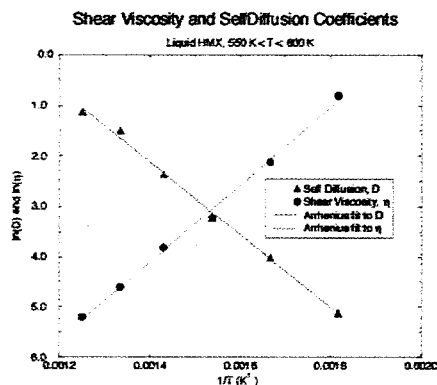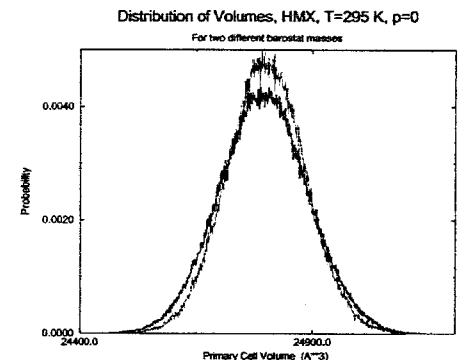 - *SCCM '01 Proceedings (Sewell et al.)*

Today...

- Elastic tensor for β-, α-, & δ-HMX (p=1 atm, T=295 K)
- Compression curve for β-, α-,& δ-HMX, 295 K, $p < 10.6$ GPa
  - Two experimental data sets for comparison in case of β-HMX
    - Olinger *et al.* ('78)
    - Yoo and Cynn ('99)
  - Path to isothermal bulk modulus K and $K'=dK/dp$
    - Requires use of EOS fitting form
      - Olinger *et al.* used Hugoniot-based form (U_s-U_p)
      - Yoo & Cynn used 3rd-order Birch-Murnaghan
      - *We use both, compare between them & with elastic tensor*
        - » See Menikoff and Sewell, High Press. Res. 21, 121 (2

Distribution of Volumes, HMX, T=295 K, p=0
For two different barostat masses

0.0040

Probability

0.0020

0.0000
24400.0   24900.0
Primary Cell Volume (A^3)

K_V=11.3 GPa
K_{Cij}=11.1 GPa
K_V=14.6 GPa

- ## This work resolves a lingering issue from previous studies
  - (1) Need to choose effective cell mass parameters in *NPT*-MD
  - (2) Apparent discrepancy $K_{fluctuations} \sim 11.5$ GPa $<< K_{isotherm} \sim 16$ GPa
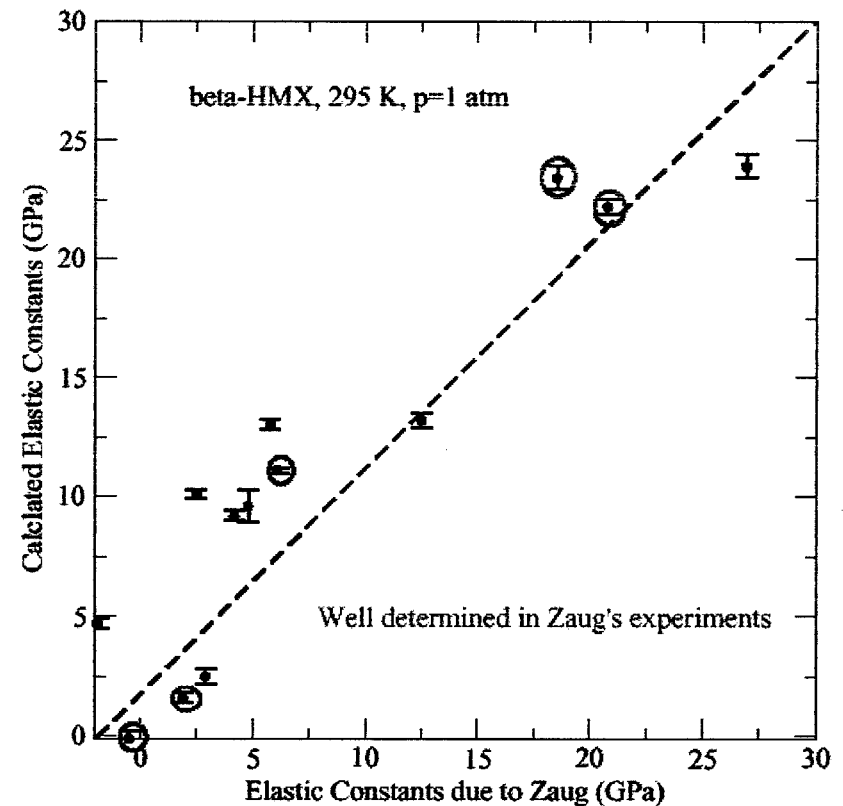
Elastic Coefficients for HMX Crystals

- Fluctuation formula for elastic tensor due to Rahman & Parrinello:

$$C_{ijkl} = \frac{\kappa T}{\langle V \rangle} \left\langle \varepsilon_{ij} \varepsilon_{kl} \right\rangle^{-1}$$

$$\varepsilon = \tfrac{1}{2}\left[h_0^{-T} \left(h^T h \right) h_0^{-1} - 1 \right]$$

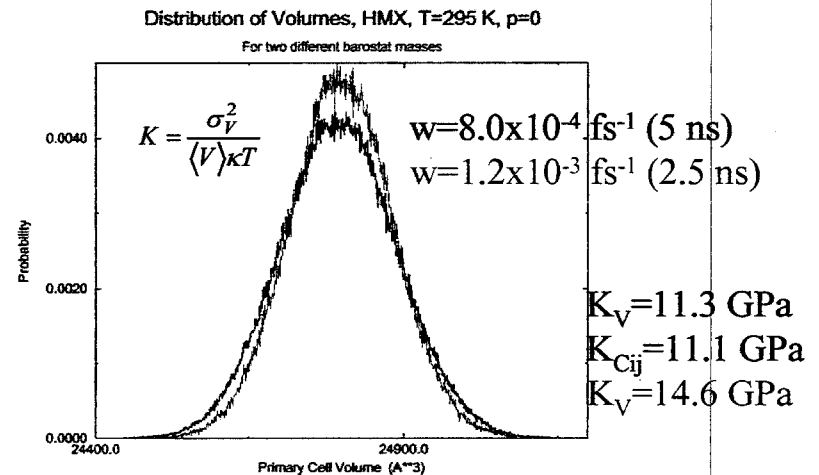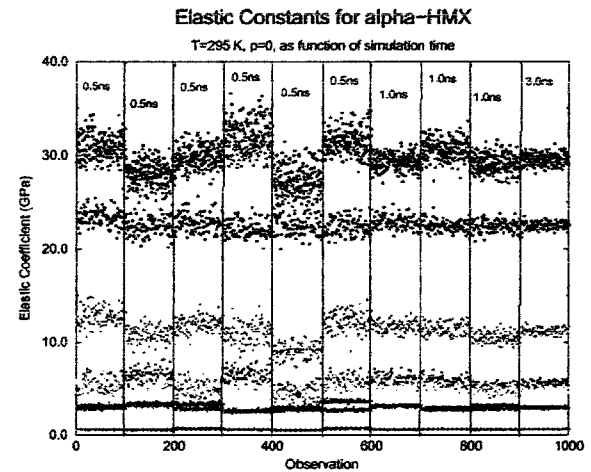- Objects readily constructed from NpT simulation

beta-HMX, 295 K, p=1 atm

Well determined in Zaug's experiments

Calclated Elastic Constants (GPa) vs Elastic Constants due to Zaug (GPa)

Elastic Tensors

HMX Polymorphs, p=1 atm, 295 K

	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	C_{15}	C_{25}	C_{35}	C_{46}
β Expt.	**20.8**	26.9	**18.5**	4.2	**6.1**	2.5	4.8	12.5	5.8	**-0.5**	-1.9	**1.9**	2.9
β N=96	22.2 (0.3)	23.9 (0.5)	23.4 (0.5)	9.2 (0.2)	11.1 (0.1)	10.1 (0.2)	9.6 (0.7)	13.2 (0.3)	13.0 (0.2)	-0.1 (0.3)	4.7 (0.2)	1.6 (0.2)	2.5 (0.3)
α N=64	30.6 (0.5)	23.3 (0.8)	31.4 (0.2)	0.80 (0.04)	3.3 (0.1)	3.3 (0.2)	5.7 (0.7)	13.8 (0.7)	6.0 (0.3)				
δ N=96	14.5 (0.7)	14.0 (0.8) C_{11}	18.0 (0.9)	4.4 (0.2)	4.4 (0.2) C_{44}	2.3 (0.4) C_{11}-C_{12}	10.3 (0.5)	10.6 (0.7)	10.3 (0.4) C_{13}				

Caveats With Calculations of C_{ij}

- Size dependence and convergence issues:
  - Finite size effects apparently not severe
  - Long simulations required to converge C_{ij}, but doable
- Barostat coupling effects?
  - Rahman-Parrinello MD includes lattice degrees of freedom
    - Must specify "cell mass" parameters; somewhat arbitrary
    - No effect on first moments, but possibly on others
  - Remedy: use NpT Monte Carlo approach!
    - Just completed, manuscript in preparation

Elastic Constants for alpha-HMX

T=295 K, p=0, as function of simulation time

Distribution of Volumes, HMX, T=295 K, p=0

For two different barostat masses

$$K = \frac{\sigma_V^2}{\langle V \rangle \kappa T}$$

$w = 8.0 \times 10^{-4}$ fs^{-1} (5 ns)
$w = 1.2 \times 10^{-3}$ fs^{-1} (2.5 ns)

$K_V = 11.3$ GPa
$K_{Cij} = 11.1$ GPa
$K_V = 14.6$ GPa

Compression Curve for β-HMX

- $0 \leq p \leq 10.6$ GPa, $T=295$ K

- $p=p(V;T) \Rightarrow K, K'$
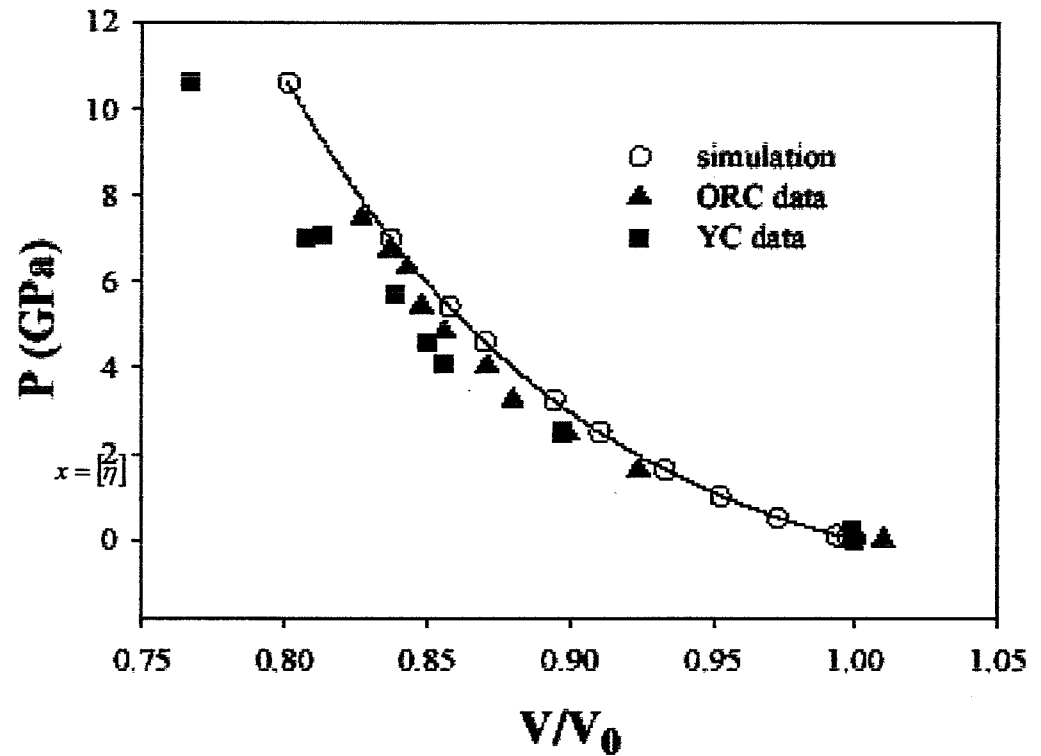 - Hugoniot-based form (Olinger *et al.*)

$$p(V) = \frac{V_0 - V}{[V_0 - s(V_0 - V)]^2} c^2$$
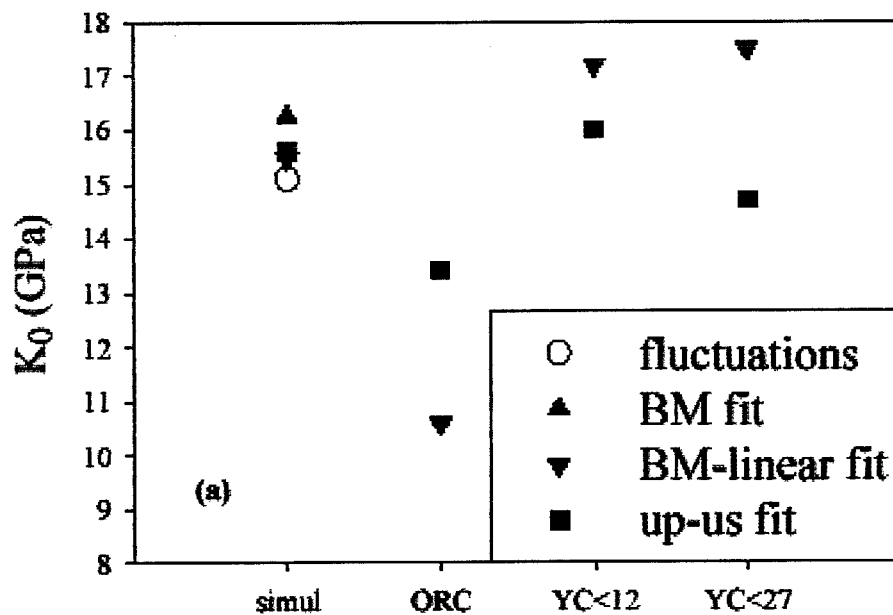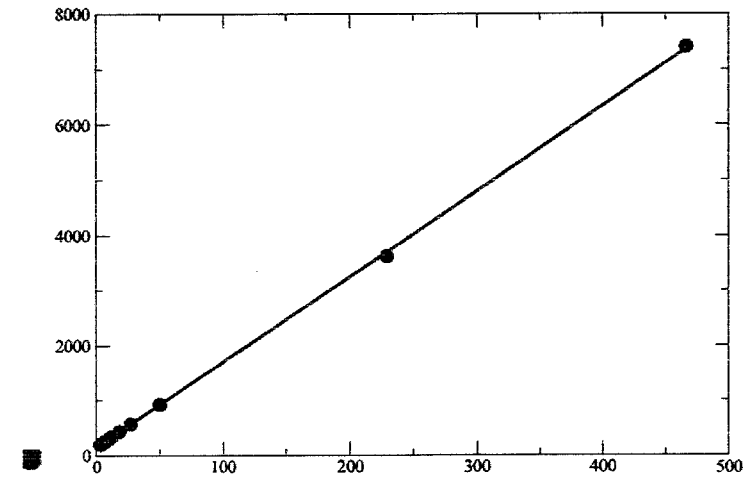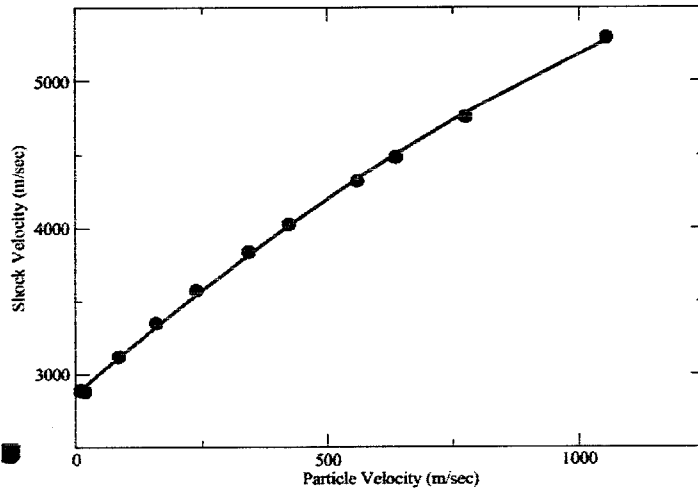
  - Birch-Murnaghan (Yoo & Cynn)

$$p(V) = \tfrac{3}{2} K \left[\eta^{-7/3} - \eta^{-5/3} \right]\left[1 + \tfrac{3}{4}\left(K' - 4\right)\left(\eta^{-2/3} - 1\right) \right]$$

y=mx+b, where x=$[\eta^{2/3}-1]^{-1}$-3 & y=2p(V)$\{3[\eta^{7/3}-\eta^{5/3}][\eta^{2/3}-1]\}^{-1}$
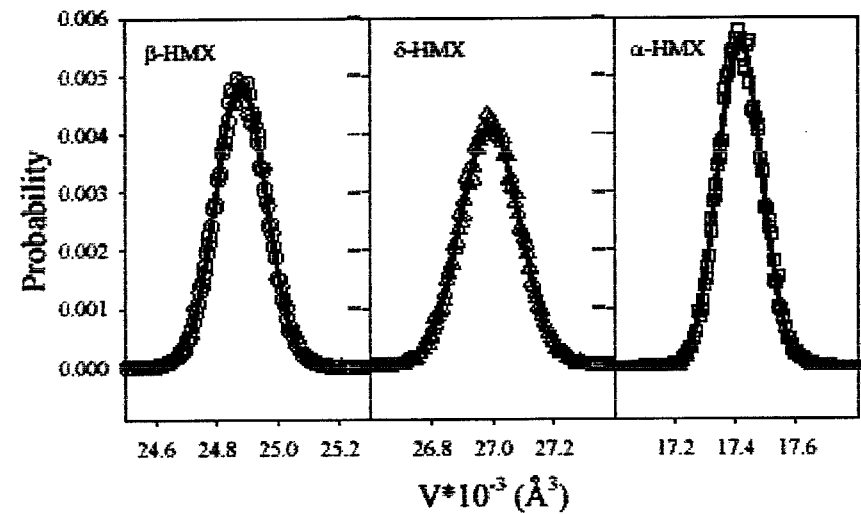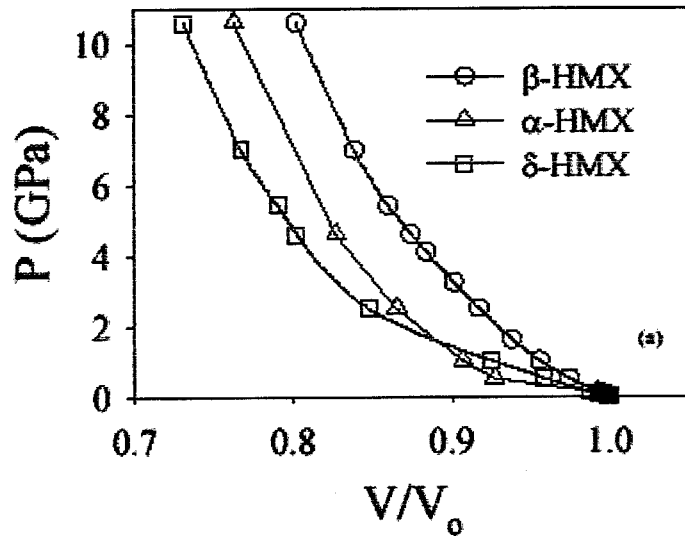*m=K, b=3KK'/4*
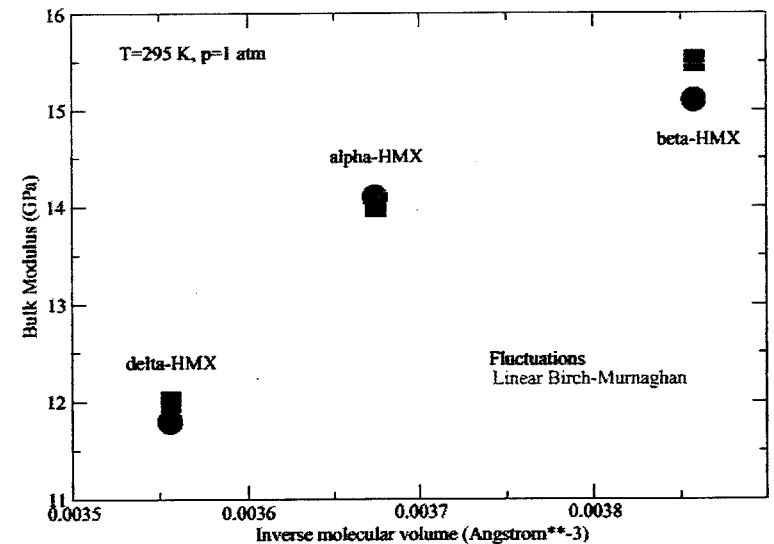
Bulk Modulus for β-HMX (1 atm, 295 K)

- Curvature in U_s-U_p plane

- Heavier weighting of low-pressure points in x-y plane (B-M)

- Consistency between bulk moduli predicted from elastic tensor and EOS fitting forms

- Good agreement with Yoo & Cynn

Isotherms and Moduli for β-, δ-, α-HMX

			α-HMX (N=64)	δ-HMX (N=96)
K (GPa)			14.1[b]	11.8[b]
			14.3[c]	11.9[c]
			14.0[d]	12.0[d]
G (GPa)			2.4[c]	2.9[c]

a. Menikoff and Sewell, High Pressure Research 21, 121 (2001).

b. From volume fluctuations:

$$K = \frac{\langle V \rangle \kappa T}{\sigma_V^2}$$

c. From elastic tensor.

d. From linear Birch-Murnaghan fit.

Preliminary Evidence for Pressure Induced Phase Transition in α-HMX
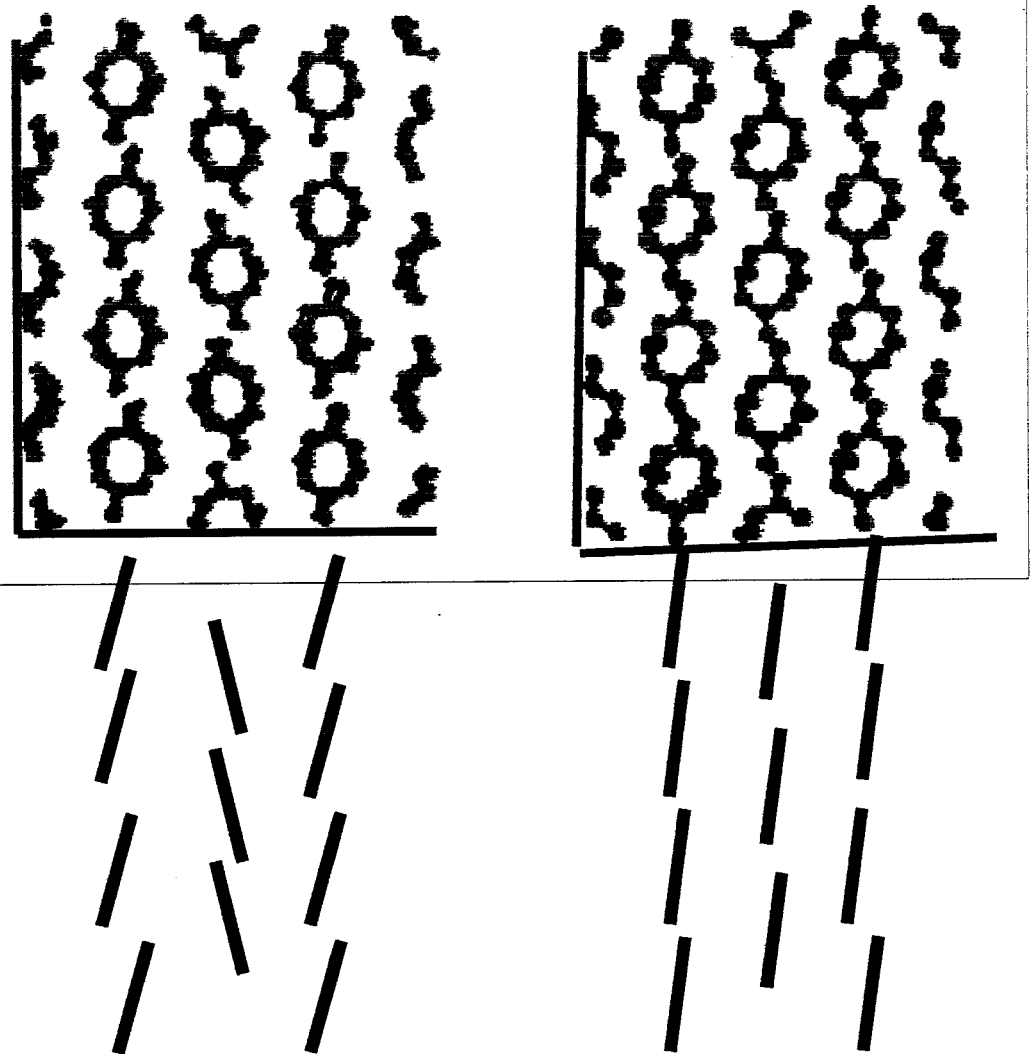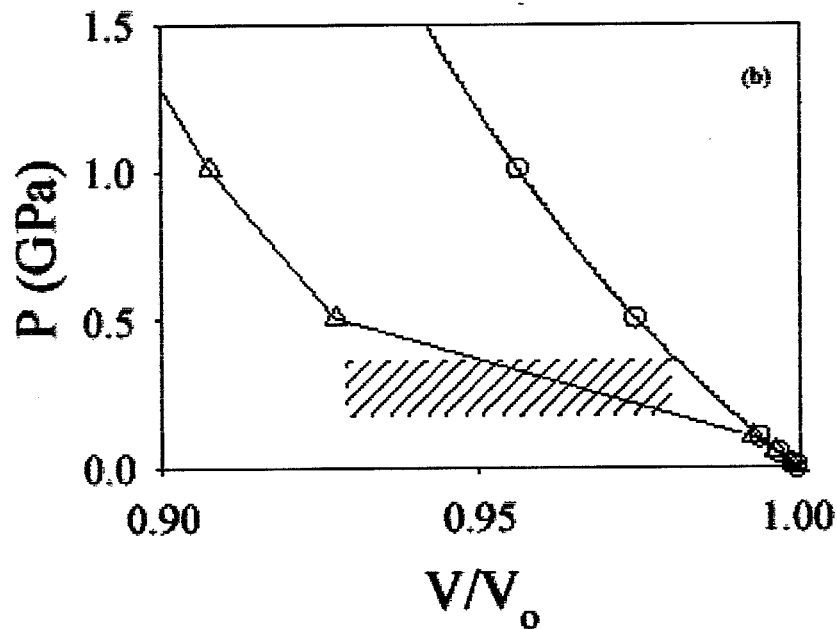
- Change in P-V slope at few kbar

- Apparent change in packing motif

- Change in lattice symmetry

- Molecular point group preserved

Ongoing & Future Work

- Contribute to mesoscale theory & simulations
  - Working on self-consistent "model mechanics and thermodynamics"
  - Seeking input from theorists & simulators concerning priorities
- Specific heat as *f(T,p)* -- *Menikoff*
  - *High priority; if one cannot predict temperature, what of chemistry?*
- Additional isotherms, elastic tensors – Mas, Baer
- Melting curve: $T_m = T_m(p)$ -- *Menikoff*
  - *Significant challenge*
- Study α-HMX pressure induced phase transition
  - Improve characterization, possibly study thermodynamics